Electro-catalytic degradation of bisphenol A with modified Co$_3$O$_4$/β-PbO$_2$/Ti electrode

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ABSTRACT

Ti-base Co$_3$O$_4$/β-PbO$_2$ composite electrodes were prepared using electro-deposition and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), cyclic voltammetry and the accelerated life testing, it indicated that the self-made electrode had high activity in electrolysis as well as excellent corrosion resistance and excellent catalytic performance. The results showed that the removal efficiency of COD$_{Cr}$ could be reached up to 92.2% after 1.5 h electrolysis at NaCl concentration of 0.020 mol·L^{-1}, bisphenol A initial concentration of 20 mg·L^{-1}, applied voltage of 20 V, electrode spacing of 7 cm and electrolyte pH of 5. The reaction mechanism and kinetics of Co$_3$O$_4$/β-PbO$_2$/Ti composite electrodes electro-catalytic degradation bisphenol A mainly caused by the OH radical attacking parent molecules and the degradation followed pseudo-first-order kinetics.

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1. Introduction

Bisphenol A (BPA) is a known endocrine disrupting chemical that is commonly used in the production of polycarbonate, epoxy resin and numerous plastic articles [1]. These final products are utilized in many foods and drink storage containers, food can linings, polycarbonate baby bottles and white dental fillings [2]. The residual BPA in bottles, due to incomplete reaction, may leach to food and ingest by human. BPA and its derivatives have been widely released to the natural environment and water during the manufacturing process and the degradation products of plastics. However, the purification of wastewater containing BPA and its derivatives is a longstanding problem owing to low rate of biodegradation. Therefore, it is quite urgent to search for a approach to degradation BPA so as to minimize its contamination [3].

Electrochemical treatment has been applied in the treatment of wastewater from electroplating, printing and dyeing, pharmaceutical and tannery industries [4]. One of the most important parts of electro-catalytic oxidation is obviously the electrode material [5]. Good electrode materials should not only be effective for pollution degradation, but also stable electrochemically and inexpensive. Up to date, β-PbO$_2$ electrodes has been extensively studied owing to its high electrical conductivity, strong oxidizing ability and low cost [6,7]. However, pure β-PbO$_2$ electrode coatings could easily flake

away from the base. Therefore, a lot of researches remain to be done to modify β-PbO$_2$ electrodes. Xue et al. [8] reported electrochemical oxidize bisphenol A with Ti/SnO$_2$-Sb$_2$O$_5$/PbO$_2$ electrode and found it could be oxidized directly on the surface of the electrode, and pH = 4 was a suitable condition for the efficient electrochemical oxidation of BPA. Pereira et al. [9] used a flow reactor with a boron-doped diamond electrode to electrochemical degrade BPA. They reported the best condition in terms of current efficiency and energy consumption occurs at 6.5 mA·cm^{-2} and 7.0 L·min^{-1}, in the absence of NaCl, when only 1.7 Ah·L^{-1} was needed to attain a 90% COD abatement. Mazzotta et al. [10] studied the electrochemical behavior of bisphenol A at PEDOT-modified glass carbon electrodes and the oxidation current was found to vary linearly with BPA concentration in the range 9.0-41 × 10^{-5} mol·L^{-1}, and the detection limit of 5.5 × 10^{-5} mol·L^{-1} was evaluated. Zaviska et al. [11] found BPA concentration could be diminished by up to 90% by applying a current intensity of 2.0 A for 100 min reaction period in the presence of 250 mg·L^{-1} Na$_2$SO$_4$ and BPA could be oxidized by both direct anodic electrochemical oxidation and indirect electrochemical oxidation via mediators.

In this paper, Co$_3$O$_4$/β-PbO$_2$/Ti composite electrodes were successfully prepared using electro-deposition. Its electro-catalytic characterization was analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and cyclic voltammetry. And composite electrodes was selected as electrode for electro-catalytic degradation of BPA simulated wastewater, the effect of initial solution pH, applied voltage and supporting electrolyte concentration on BPA degradation were systematically investigated. In order to

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provide theoretical and technical reference for improvement of electrodes and treatment of BPA, the degradation kinetics and mechanisms of BPA were preliminary discussed.

2. Experimental

2.1. Chemicals and instruments

2.1.1. Chemicals

Bisphenol A (Sinopharm Chemical Reagent Co., Ltd.), tertiary butanol, silver sulfate (Tianjin Damao Chemical Reagent Factory), lead dinitrate, ammonium iron sulfate, mercuric sulfate, sodium chloride and oxalic acid (Shantou Xilong Chemical Reagent Factory), potassium dichromate (Shanghai Surui Chemical Reagent Co, Ltd.), sulfuric acid and phosphoric acid (Shanghai Zhengqi Chemical Reagent Co. Ltd.), all of chemical were analytical grade reagent and used as received.

2.1.2. Electrochemical characterization analytical instruments

Electrochemical workstation (CHI 660C, Shanghai Zhenhua Instrument Co. Ltd.), DC Power Supply (WYK-1503, Jiangsu Powerware Electric Manufacturing Co., Ltd.), pH meter (DELTA-320, Mettler Toledo Instrument Co., Ltd.).

2.1.3. Physical characterization analytical instruments

Scanning electron microscopy (Acquity UPLC LCT Premier TM XE, Waters), X-ray diffractometer analyzer (DX-2700 X ray diffractometer analyzer, copper electrode target, graphite monochromator, tube voltage of 40 kV, scanning rate of 6°/min and sampling interval of 0.02°, Shanghai precision instruments and meters Co. Ltd.), Atomic absorption spectrometer (WFX-130A, Beijing Rayleigh Analytical Instrument Co. Ltd) and UV–vis absorption spectrometry (UV-175, Shimadzu).

Cyclic voltammetry curve was tested with standard three-electrode cell. The self-made electrode served as target electrode, Pt as auxiliary electrode, and standard saturated calomel electrode as reference electrode. The cyclic voltammetry curve was examined in 0.5 mol·L^{-1} H$_2$SO$_4$ solution with a scan rate of 100 mV·s^{-1}.

2.2. Electrode preparation

2.2.1. Titanium plate pretreatment

The Co$_3$O$_4$/β-PbO$_2$/Ti electrodes were prepared using a standard electro- deposition technique on Ti plates. The dimensions of Ti plates were 5 cm × 10 cm × 0.2 cm and the effective area was 5 cm × 5 cm. Prior to deposition process, the Ti plates were polished with sand paper and then cleaned using ultrasound to remove sand particles lodged in the metal. Then, Ti plates were degreased in 40% NaOH for 20 min, followed by thoroughly washing with deionized water, and then stewed in 10% oxalic acid solution for 2 h until oxalic acid titanium formed on Ti plate surface. After these pretreatment, Ti plates were stored in 1% oxalic acid solution [12,13].

2.2.2. Co$_3$O$_4$/β-PbO$_2$/Ti preparation

The Ti plate stored in 1% oxalic acid solution was rapidly inserted into electrodeposition solution mixture containing 0.1 mol·L^{-1} HNO$_3$, 5 mmol·L^{-1} Co$_3$O$_4$ and 0.5 mol·L^{-1} Pb(NO$_3$)$_2$. The cathode was Ti plate with the same area. The applied current density was 20 mA·cm^{-2} and different thickness Co$_3$O$_4$/β-PbO$_2$/Ti obtained by proper electro-deposition time [13].

2.2.3. Electro-catalytic performance of Co$_3$O$_4$/β-PbO$_2$/Ti

The electro-catalytic activity of the Co$_3$O$_4$/β-PbO$_2$/Ti electrode was evaluated by the decomposition of BPA in an electrochemical cell with an effective volume of 360 mL (12 cm × 6 cm × 5 cm).

The Co$_3$O$_4$/β-PbO$_2$/Ti and Ti plate were employed as anode and cathode for electro-catalytic decomposition of BPA aqueous solution. Cathodic effects were of minor importance for the reactions considered here. The electrolytic cell was made by PTFE material. Experimental setup adopted opposite side for electrode and cathode.

To start the experiment, a certain amount of BPA aqueous solution was placed in electrolytic cell. The Co$_3$O$_4$/β-PbO$_2$/Ti plate was used as anode and the Ti plate as cathode. The removal of BPA resulted in the change of solutes composition in solution and accordingly the change of chemical oxidation demands (COD$_{Cr}$). Therefore, COD$_{Cr}$ in solution before and after electrolyzing were chosen as the parameter to evaluate the process of electro-catalytic degradation. COD$_{Cr}$ removal efficiency was calculated as:

$$COD(\%) = \frac{[COD_{Cr}]_0 - [COD_{Cr}]}{[COD_{Cr}]_0} \times 100\%$$

Where [COD$_{Cr}$]$_0$ and [COD$_{Cr}$] were determined by potassium dichromate titration before and after electrolyzing for time t, respectively.

3. Results and discussion

3.1. Characterization of Co$_3$O$_4$/β-PbO$_2$/Ti electrode analysis

3.1.1. SEM characterization

Scanning electron microscopy (SEM) micrographs of β-PbO$_2$/Ti electrode (a) and Co$_3$O$_4$/β-PbO$_2$/Ti electrode (b) with magnification of 3000 times were shown in Fig. 1, the cobalt oxides thickness of β-PbO$_2$ and Co$_3$O$_4$/β-PbO$_2$ coating were about 28.50 and 27.88 μm, respectively and the morphology of both samples was rather similar. However, β-PbO$_2$/Ti electrode had a uniform composition and a pyramidal cluster distribution. Compared with the β-PbO$_2$/Ti electrode, Co$_3$O$_4$/β-PbO$_2$/Ti electrode had a small size crystal particles and a very compact crystalline structure. And Co$_3$O$_4$/β-PbO$_2$/Ti electrode had some un-regular shape of Co$_3$O$_4$ particles. It was obvious that the structure of the Co$_3$O$_4$/β-PbO$_2$/Ti will provide more specific surface and better physical performance for the electro-catalytic degradation of BPA.

3.1.2. XRD characterization

The XRD patterns of β-PbO$_2$/Ti electrode (c) and Co$_3$O$_4$/β-PbO$_2$/Ti electrode (d) were shown in Fig. 1. It demonstrated that the characteristic reflections of β-PbO$_2$ with three crystal planes at 25.4°, 32°, 49.1°, respectively. After adding Co$_3$O$_4$, the electrode crystallization was mainly unchanged and it was still the β-PbO$_2$. But unlike β-PbO$_2$, the changes of peak intensities for the different crystal planes was observed [5,13].

3.1.3. Cyclic voltammetry curve

The cyclic voltammetry curve obtained with Co$_3$O$_4$/β-PbO$_2$/Ti electrode in 0.5 mol·L^{-1} H$_2$SO$_4$ solution containing 20 mg·L^{-1} BPA was shown in Fig. 1d. The scanning range was between 0 and 2.0 V. The Co$_3$O$_4$/β-PbO$_2$/Ti electrode oxygen evolution potential was about 1.73 V, this high oxygen evolution indicated oxygen formation was not easily took place on Co$_3$O$_4$/β-PbO$_2$/Ti electrodes [13–15]. In the reversed potential scan, a reduction peak between 1.3 and 1.4 V. Reduction peak may correspond to the generation of Pb^{2+} from PbO$_2$ [16]. There was no oxidation peak appeared in Fig. 1d, which indicated that the BPA was not directly oxidized on Co$_3$O$_4$/β-PbO$_2$/Ti electrode but indirectly oxidized. PbO$_2$ electrode belongs to "nonnative electrode" [14]. Thereby, BPA degradation was attributed to indirect oxidation degradation of active active radical (such as OH·) and intermediate products produced in electrolytic process [5].